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(54) Catalysts for the purification of waste gases

(57) A catalyst for the purification of waste gas by the removal of nitrogen oxides comprises (A) from 80 to 95% by weight of an oxide obtained by thermal treatment of a binary hydrous oxide of titanium and silicon, a binary hydrous oxide of titanium and zirconium or a ternary hydrous oxide of titanium, zirconium and silicon in the presence of sulfuric acid or ammonium sulfate, (B) from 0 to 5% by weight of vanadium oxide, and (C) from 1 to 15% by weight of an oxide of tungsten, molybdenum, tin or cerium.

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SPECIFICATION
Purification of Waste Gases

The invention relates to catalysts for the purification of waste gases such as exhaust gas by the removal of nitrogen oxides. Such gases emanate from boilers and similar stationary combustors at thermal power

5 plants, iron foundries and like plants. In such gases, nitrogen oxides (mainly NO and NO₂; herein designated "NO_x"), sulfur oxides (containing mainly sulfur dioxide; herein designated "SO_x") with ammonia added as a reducing agent, are decomposed by catalysts into nitrogen and water, and the oxidation of sulfur dioxide into sulfur trioxide is low.

The invention provides a catalyst for the purification of waste gas removal of nitrogen oxides which 10 comprises (A) from 80 to 95% by weight of an oxide obtained by thermal treatment of a binary hydrous oxide of titanium and silicon, a binary hydrous oxide of titanium and zirconium or a ternary hydrous oxide of titanium, zirconium and silicon in the presence of sulfuric acid or ammonium sulfate, (B) from 0 to 5% by weight of vanadium oxides, and (C) from 1 to 15% by weight of an oxide of tungsten, molybdenum, tin or cerium. A mixture of two or more of any of the groups of compounds listed may of course be used.

15 Binary oxides of titanium and silicon (herein designated TiO₂-SiO₂) are known from Ito, M., Hattori, H. and Tanabe, K., J. Catal., 35, 225—231 (1974), to be solids which exhibit an acidity not observed in either of the component oxides, and have a large surface area. TiO₂-SiO₂ is not a mere mixture but a composite oxide. Binary composite oxides of titanium and zirconium (herein designated TiO₂-ZrO₂) and ternary composite oxides of titanium, zirconium and silicon (TiO₂-ZrO₂-SiO₂) possess properties similar to 20 TiO₂-SiO₂. It has been already disclosed in our patent Specification U.S. 4,221,768 that these composite oxides produce a catalyst which has a high NO_x removal power, lower ability to oxidize SO₂ but outstanding durability.

We have now found according to the present invention a catalyst which has a high NO_x removal power, low ability to oxidize SO₂, outstanding thermal resistance, durability and moldability. This is produced by 25 thermal treatment of a hydrous oxide precursor of TiO₂-SiO₂, TiO₂-ZrO₂ or TiO₂-ZrO₂-SiO₂ before calcination in the presence of sulfuric acid and/or ammonium sulfate to yield TiO₂-SiO₂-S, TiO₂-ZrO₂-S or TiO₂-ZrO₂-SiO₂-S. These sulphur-containing composite oxides have properties similar to TiO₂-SiO₂, TiO₂-ZrO₂ and TiO₂-ZrO₂-SiO₂. They are solid acids and have large surface area. By X-ray diffraction analysis, they are shown to have an amorphous structure. They have a solid acid distribution involving fewer points of strong 30 acidity and more points of weak acidity than TiO₂-SiO₂, TiO₂-ZrO₂ and TiO₂-ZrO₂-SiO₂. Points of strong acidity in the catalyst are believed to impede NO_x removal because they adsorb ammonia. Thus these sulphur-containing composite oxides can each be used as component (A) in a catalyst according to the invention.

When SiO₂ is present in the form of TiO₂-SiO₂-S in the component (A) an increase in the SiO₂ content 35 causes hardly any decrease in the NO_x removal; rather it suppresses sulfur dioxide oxidation.

Vanadium oxide, tungsten oxide and other catalyst components are stably retained in a highly dispersed state in component (A) of the catalyst of the invention, which therefore has a higher resistance to heat than catalysts in which these components have been mixed homogeneously, for example, by co-precipitation. When used for a long time at elevated temperatures, the active components of catalysts 40 according to the invention are hardly sintered by the heat and their physical properties are only affected minimally. The catalyst exhibits high NO_x removal activity and low ability to oxidize sulfur dioxide despite a relatively low vanadium oxide content. It is resistant to acids, refrains from yielding to the action of SO_x and halide, manifests stable NO_x removal ability for a long time, and can be mass produced as a good quality product in high yield because of its excellent moldability.

45 In atomic percentages, the component (A) is desirably composed of from 40 to 95%, preferably from 50 to 90%, of titanium, from 5 to 60%, preferably 10 to 50%, of silicon and/or zirconium, and from 1.2 to 7%, preferably 1.5 to 5%, of sulfur. The NO_x removal activity of the catalyst is insufficient, generally speaking, if titanium accounts for less than 40% and silicon and/or zirconium account for 60% or more. If titanium accounts for more than 95% and silicon and/or zirconium accounts for less than 5%, the ability to oxidize 50 SO₂ is enhanced to an undesirable extent. In the aforementioned atomic percentages, the total of titanium and silicon and/or zirconium and sulfur is 100. If sulfur accounts for less than 1.2% in atomic percentage, no solid acid distribution is obtained and the activity is diluted. If sulfur accounts for more than 7%, the NO_x removal at temperatures below 300°C is insufficient, and the moldability of the catalyst is inferior. Thus, the sulfur content in atomic percentage is desirably from 1.2 to 7%.

55 If the temperature at which the thermal treatment is performed is lower than 450°C, the catalyst has inferior resistance to heat. If this temperature exceeds 700°C, the solid acidity is degraded, and the ability to oxidize SO₂ is enhanced. This temperature is preferably from 450° to 700°C, more preferably from 500° to 650°C. The resulting sulfur-containing composite oxides possess an amorphous structure or a crystalline structure approaching an amorphous structure as determined by the X-ray diffraction, and a BET 60 (Brunauer-Emmett-Teller) surface area of not less than 60 m²/g, preferably from 80 to 250 m²/g.

For the preparation of the sulfur-containing composite oxides, the titanium source may be an inorganic titanium compound such as titanium chloride, titanium sulfate or titanium hydroxide, or an organic titanium compound such as titanium oxalate or tetrakisopropyl titanate. The silicon source may be an inorganic silicon compound such as colloidal silica, water glass or silicon tetrachloride, or an organic silicon

compound such as ethyl silicate. The zirconium source may be an inorganic zirconium compound such as zirconium chloride, zirconium oxychloride, zirconium sulfate, zirconium oxysulfate or an organic zirconium compound such as zirconium oxalate or tetraisopropyl zirconate. The ammonium sulfate may be derived from ammonium hydrogen sulfate and ammonium sulfite.

5 TiO_2-SiO_2-S is advantageously prepared by neutralizing an aqueous ammonia solution containing silica 5
sol with a sulphuric acid solution of titanyl sulfate or an aqueous solution of titanium tetrachloride. A precipitate is produced, washed, and dried at from 100° to 250°C. TiO_2-SiO_2 powder is formed as a hydrous oxide compound, and added to an aqueous solution of ammonium sulfate or an aqueous solution of sulfuric acid. The resultant combination is thoroughly mixed, immediately concentrated, dried and calcined

10 at from 450° to 700°C. 10

In greater detail: Either an aqueous sulfuric acid solution of titanyl sulfate or an aqueous titanium tetrachloride solution containing an appropriate amount of titanium is prepared in a concentration of from 1 to 100 g/liter as titanium oxide. Separately, an aqueous solution of silica sol containing an appropriate amount of silica, by addition of ammonia of the amount required for neutralization, is prepared in a

15 concentration of 1 to 100 g/liter of silica. To this aqueous solution, while under agitation, the 15
aforementioned aqueous solution of titanyl sulfate or aqueous solution of titanium tetrachloride is gradually added. There is a gradual liberation of the heat of neutralization which induces formation of a coprecipitate containing titanium and silicon. This coprecipitate is separated off by filtration, washed, dried at from 100° to 250°C for from 1 to 10 hours, and pulverized. The dry TiO_2-SiO_2 powder thus produced

20 generally contains from 0.1 to 8% by weight of sulfur oxide as SO_4^{2-} , and from 10 to 30% by weight of water 20
when the sulfate solution of titanyl sulfate is used as the starting material. Since this sulfur component does not remain in a stable state, the dry powder requires a further addition of a sulfuric acid or ammonium sulfate. The TiO_2-SiO_2 hydrous oxide gives good results particularly when the sulfur oxide content falls to from 5 to 20% by weight, preferably from 9 to 15% by weight, as SO_4^{2-} . The hydrous oxide may

25 alternatively be prepared by incorporating the desired amount of sulfur compound into a slurry of a 25
coprecipitated compound obtained by neutralization with ammonia.

The dry powder of TiO_2-SiO_2 is calcined preferably for from 5 to 10 hours to obtain TiO_2-SiO_2-S powder containing the desired amount of sulfur. TiO_2-ZrO_2-S and $TiO_2-ZrO_2-SiO_2-S$ can be prepared similarly.

As regards the catalyst components (B) and (C), the starting material may be an oxide, hydroxide, 30
inorganic acid salt or organic acid salt, particularly ammonium salt, oxalate, nitrate, sulfate or halide.

The catalyst preferably comprises by weight percentages of each of the components as follows: from 85 to 95% of (A), from 0 to 3% of (B), from 3 to 12% of (C). If (B) accounts for more than 5%, the ratio of 30
oxidation of sulfur dioxide increases and the catalyst becomes unfit for NO_x removal from an exhaust gas containing sulfur dioxide in a high concentration. If the proportion of (C) is outside the aforementioned

35 range, the NO_x removal is reduced or the cost of raw materials is raised. 35

A typical procedure for the preparation of the catalyst follows: Where the catalyst is to contain TiO_2-SiO_2-S , vanadium, and tungsten, prescribed amounts of ammonia meta-vanadate and ammonium para-tungstate are dissolved in an aqueous solution of monoethanolamine or oxalic acid. The resultant 40
aqueous solution containing vanadium and tungsten is kneaded with the TiO_2-SiO_2-S powder prepared in
advance by the aforementioned procedure and a molding aid, and molded into the shape of honeycomb by 40
an extrusion molder. The molder blend is dried at from 50° to 120°C and then calcined at from 300° to 650°C, preferably from 350° to 550°C for from 1 to 10 hours, preferably from 2 to 6 hours under a current of air to produce a catalyst. Alternatively, the TiO_2-SiO_2-S powder may be molded into the shape of honeycomb, calcined and impregnated with an aqueous solution containing vanadium and tungsten.

45 The preparation of the catalyst may involve use of a carrier. Examples of suitable carriers include 45
alumina, silica, silica-alumina, bentonite, diatomaceous earth, silicon carbide, titania, zirconia, magnesia, cordierite, mullite, pumice, activated carbon and inorganic fibers. Such a carrier may be blended with the catalyst or carry the catalyst thereon.

The shape of the catalyst is not limited to the honeycomb. It may be a circle, column, cylinder, plate, 50
ribbon, corrugated plate, pipe, doughnut, or lattice for example.

The waste gas to be treated is generally an exhaust gas which contains from 10 to 2,000 ppm of SO_x , 1 to 20% by volume of oxygen, 1 to 15% by volume of carbon dioxide, 5 to 15% by volume of steam, 0.01 to 30 g of dust per Nm^3 and 50 to 1,000 ppm of NO_x (mainly NO). The catalyst is capable of treating 50
 NO_x -containing exhaust gases containing no SO_x , NO_x -containing exhaust gases containing halogen compounds and other special exhaust gases. The conditions of treatment vary with the kind and behaviour 55
of the particular exhaust gas. The amount of ammonia (NH_3) to be added is desirably from 0.5 to 3 parts per part of NO_x . In the exhaust gas from a boiler, for example, since the greater part of NO_x is NO, the amount of ammonia to be added should be such that the molar ratio of NO to NH_3 is about 1:1. Special attention must otherwise be paid to preventing excess NH_3 from release into the ambient air. Where excess NH_3 must be

60 repressed to the fullest extent, the amount of ammonia to be added is desirably such that the molar ratio of NH_3/NO is below 1. Then, the reaction temperature is desirably from 150° to 550°C, preferably from 200° to 450°C. The space velocity is advantageous from 1,000 to 100,000 hr^{-1} , preferably from 3,000 to 30,000 hr^{-1} . The pressure is desirably from 0.01 to 10 kg/cm^2 . The reactor may be of fixed-bed type, moving-bed type or fluidized-bed type for example.

EXAMPLE 1

An aqueous sulfuric acid solution of titanyl sulfate having the following composition was used as a titanium source:

	TiOSO ₄ (as TiO ₂)	250 g/liter	
5	total H ₂ SO ₄	1100 g/liter	5

Separately, 400 liters of water was mixed with 286 liters of aqueous ammonia (NH₃ 25%) and 24 kg of silica sol (a produce having a SiO₂ content of about 30% by weight, manufactured by Nissan Chemical Kabushiki Kaisha and marketed under the Trademark Snowtex -30) was added to the resultant solution. Into the solution thus obtained, under agitation, a titanium-containing aqueous sulfuric acid solution obtained by 10 diluting 153 liters of the aqueous sulfuric acid solution of titanyl sulfate with 300 liters of water was gradually added dropwise to produce a coprecipitate gel. The solution containing the coprecipitate was left standing for 15 hours. The gel thus obtained was separated by filtration, washed with water, and dried at 200°C to 10 hours. The hydrous oxide compound was found to contain 3.0% by weight of sulfur as SO₄²⁻ and 16% by weight of water. 15 The hydrous oxide compound thus obtained was mixed thoroughly with 100 liters of an aqueous ammonium sulfate solution containing 3.1 kg of ammonium sulfate. The resultant mixture was concentrated, dried to hardness, and calcined at 550°C for 6 hours in an atmosphere of air. The powder produced had a composition of Ti:Si:S=78.5:18.4:3.1 (atomic ratio) and a BET surface area of 180 m²/g, and will be designated TSS-1. 20 0.7 liter of monoethanolamine was mixed with 7 liters of water. 2.12 kg of ammonium para-tungstate was dissolved in the resultant solution followed by 0.468 kg of ammonium meta-vanadate to obtain a homogeneous solution. In a kneader, this solution and 16 kg of TSS-1 were thoroughly mixed with a gradual addition of a suitable amount of water. The resultant blend was molded by extrusion into the shape of a lattice 80 mm square outside section, 4.0 mm square mesh, 1.0 mm wall thickness and 500 mm length. 25 The molded blend was dried at 60°C and calcined at 400°C for 5 hours under a current of air. The catalyst had a composition of TSS-1:V₂O₅:WO₃=88:2:10 as oxides by weight ratio.

EXAMPLE 2

A hydrous oxide (having a water content of 19% by weight) was obtained following the first paragraph of Example 1, except that 400 liters of an aqueous titanium tetrachloride solution containing 90.83 kg of 30 titanium tetrachloride was used as the titanium source. The hydrous oxide thus obtained was stirred in 100 liters of an aqueous sulfuric acid solution containing 5.3% by weight of sulfuric acid. The resultant mixture was concentrated dried to hardness, and calcined at 550°C for 6 hours in an atmosphere of air. The powder obtained was found to have a composition of Ti:Si:S=78.4:18.8:2.8 (atomic ratio) and a BET surface area of 170 m²/g, and will be designated TSS-2. A lattice-shaped catalyst was prepared from TSS-2 by following the 35 last paragraph of Example 1. The catalyst had a composition of TSS-2:V₂O₅:WO₃=88:2:10 as oxides by weight ratio.

EXAMPLE 3

19.3 kg of zirconium oxychloride (ZrOCl₂ · 8H₂O) was dissolved in 1000 liters of water. The resultant solution was thoroughly mixed with 78 liters of the solution of titanyl sulfate used as the titanium source in 40 Example 1. To the solution formed, under thorough agitation, with the temperature kept at about 30°C, aqueous ammonia was added dropwise until the pH became 7. The mixture produced was left standing for 15 hours. The TiO₂-ZrO₂-S gel obtained was separated by filtration, washed with water and dried at 200°C for 10 hours.

The hydrous oxide produced was thoroughly mixed with 100 liters of an aqueous ammonium sulfate 45 solution containing 1.01 kg of ammonium sulfate, concentrated, dried to hardness and calcined at 500°C for 6 hours in an atmosphere of air. The powder produced had a composition of Ti:Zr:S=78.3:19.2:2.5 (atomic ratio) and a BET surface area of 140 m²/g, and will be designated TZS-1.

A lattice-shaped catalyst was produced from TZS-1 by following the last paragraph of Example 1. The finished catalyst had a composition of TZS-1:V₂O₅:WO₃=88:2:10 as oxides by weight ratio.

50 EXAMPLE 4
TiO₂-ZrO₂-SiO₂-S powder was prepared by combining the procedures of Examples 1 and 3. The powder produced had a composition of Ti:Zr:Si:S=78.4:4.0:14.0:3.2 (atomic ratio) and a BET surface area of 170 m²/g, and will be designated TZSS-1. A lattice-shaped catalyst was prepared from TZSS-1 by following the last paragraph of Example 1. The finished catalyst had a composition of TZSS-1:V₂O₅:WO₃=88:2:10 as 55 oxides by weight ratio.

Industrial Application

The catalysts obtained in Examples 1 to 4 were tested for NO_x removal efficiency and conversion of SO₂ to SO₃: A lattice-shaped catalyst (4.0 mm square mesh and 1.0 mm wall thickness) was cut into 16 mm

square area and piled up to 500 mm in height. A stainless steel reaction tube 38 mm in inside diameter immersed in a molten salt bath was packed with the catalyst. A synthetic boiler exhaust gas of the composition set out below was mixed with ammonia and introduced into the catalyst bed at a flow rate of 0.894 Nm³/Hr (space velocity 7,000 hr⁻¹). In the ensuing reaction, the catalyst was tested for NO_x removal at 5 300° to 380°C and for conversion of SO₂ to SO₃ at 350°C.

5

Gas Composition	
NO	200 ppm
SO ₂	800 ppm
O ₂	4% by volume
NH ₃	200 ppm
CO ₂	10% by volume
H ₂ O	ca. 10% by volume
N ₂	Balance

10

10

15 NO_x removal was determined by measuring the NO_x concentrations of the gas at the inlet and outlet of the catalyst bed with a NO_x meter (chemiluminescence type, produced by Kabushiki Kaisha Yanagimoto Seisakusho and marketed under Trademark ECL-7S) and applying the results of measurement to the following formula.

15

$$\text{NO}_x \text{ removal efficiency (\%)} = \frac{\text{NO}_x \text{ concentration at the inlet} - \text{NO}_x \text{ concentration at the outlet}}{(\text{NO}_x \text{ concentration at the inlet})} \times 100$$

20 The SO₂ conversion was determined by causing the total SO_x in the exhaust gas at the outlet of the catalyst bed to be adsorbed by a 5% aqueous hydrogen peroxide solution for a fixed length of time, collecting the total SO_x in the form of an aqueous sulfuric acid solution, weighing out part of the aqueous solution with isopropyl alcohol, titrating the resultant mixture with an aqueous barium acetate solution adjusted in advance to a prescribed concentration with Arsenazo III as an indicator, collecting the SO₃ in the exhaust gas as sulfuric acid by the method proposed in H. Goksyu et al: J. Ins. Fuel., Vol 35, p. 177, 1961, 25 finding the SO₃ concentrated, and applying the results to the following formula.

20

$$\text{SO}_2 \text{ conversion (\%)} = \frac{(\text{SO}_3 \text{ concentration at the outlet})}{(\text{Total SO}_x \text{ concentration})} \times 100$$

the results are shown in Table 1.

30

30

TABLE 1
NO_x removal efficiency (%) at reaction temperature of SO₂ conversion (%) at reaction temperature of

Catalyst	300°C	350°C	380°C	350°C
Example 1	92	96	97	0.6
Example 2	92	96	97	0.6
Example 3	90	94	95	0.6
Example 4	91	95	96	0.5

35

35

These results indicate that the catalysts possess high NO_x removal power and low ability to oxidize SO₂, indicating that the catalysts excel in performance.

EXAMPLES 5—10

40 Various TiO₂-SiO₂-S powders indicated in Table 2 were prepared by using catalyst components (A) of dissimilar compositions to produce catalysts having a fixed composition of (TiO₂-SiO₂-

40

S):V₂O₅:WO₃=88:2:10 (weight ratio) by following the procedures of Examples 1 and 2. The results were tested for catalytic properties as above, and the results are shown in Table 2.

EXAMPLE 11

A hydrous oxide was obtained by following the first paragraph of Example 1, except that 400 liters of an aqueous titanium tetrachloride solution containing 90.83 kg of titanium tetrachloride was used as the titanium source. It was calcined at 550°C for 6 hours in an atmosphere of air. The powder produced will be designated TS-1. In 7 liters of water, 2.8 kg of oxalic acid and 2.12 kg of ammonium para-tungstate were dissolved followed by 0.939 kg of vanadyl sulfate (VOSO₄ · 4H₂O) to form a homogeneous solution. By mixing this solution with 16 kg of TS-1 and processing the resultant mixture by following the last paragraph of Example 1, there was produced a lattice-shaped catalyst. The finished catalyst was found to have a composition of TS-1:V₂O₅:WO₃=88:2:10 as oxides by weight ratio. This catalyst was tested for catalytic properties as above, and the results are shown in Table 2.

EXAMPLE 12

Titanium hydroxide gel was obtained from 400 liters of an aqueous titanium tetrachloride solution containing 90.83 kg of titanium tetrachloride (TiCl₄) by lowering the pH to 7 by addition of aqueous ammonia, separating the precipitate formed by filtration, and washing the precipitate with water. Separately, 0.7 liter of monoethanolamine and 7 liters of water were mixed and 2.12 kg of ammonium paratungstate and 0.468 kg of ammonium meta-vanadate were dissolved in the resultant solution. Then, 24 kg of silica sol (Snowtex-30) was added to produce a homogeneous solution. The titanium hydroxide gel was thoroughly mixed with this solution. The resultant mixture was concentrated, dried to hardness, dried at 200°C for 10 hours, and calcined at 500°C for 3 hours in an atmosphere of air. The catalyst powder so obtained was molded following the last paragraph of Example 1 to produce a lattice shaped catalyst. The finished catalyst was found to have a composition of (TiO₂+SiO₂):V₂O₅:WO₃=88:2:10 as oxides by weight ratio. The catalyst was tested by following the procedure above, and the results are shown in Table 2.

25

TABLE 2
TiO₂-SiO₂-S composition

Catalyst	Ti:Si:S (atomic ratio)	300°C	NO _x removal efficiency (%) at reaction temperature of			SO ₂ conversion (%) at reaction temperature of 350°C
			350°C	380°C		
Example 5	78.8:19.5:1.7	92	96	97		0.6
Example 6	78.6:17.4:4.0	91	96	97		0.6
Example 7	64.7:30.2:5.1	90	95	96		0.5
Example 8	77.1:16.4:6.5	90	96	97		0.8
Example 9	80.0:19.7:0.5	90	94	95		0.6
Example 10	76.5:16.5:10.0	84	93	94		1.2
Example 11	80.0:20.0:0	85	93	94		0.6
Example 12	80.0:20.0:0	78	86	87		1.0

The results of Table 2 show that the catalysts possessed high NO_x removal and low SO₂ oxidizing activity.

EXAMPLES 13—16

Various catalysts were prepared by following the procedure of Example 1 using the TSS-1 and varying the components (A). As raw materials for the catalyst, ammonium salts of vanadium, tungsten and molybdenum, a chloride of tin, and a nitrate of cerium were used. The catalyst compositions and results are shown in Table 3.

TABLE 3
 NO_x removal
 efficiency (%)
 at reaction
 temperature of
 300°C 350°C 380°C SO_2 conversion
 (%) at reaction
 temperature of
 350°C

5	Catalyst	Composition (weight ratio)	300°C	350°C	380°C	5
	Example 13	TSS-1: $\text{V}_2\text{O}_5:\text{WO}_3$ =89:1:10	90	95	96	0.3
10	Example 14	TSS-1: $\text{V}_2\text{O}_5:\text{MoO}_3$ =88:2:10	92	96	97	0.7
	Example 15	TSS-1: $\text{V}_2\text{O}_5:\text{SnO}_2$ =93:2:5	92	95	96	0.6
	Example 16	TSS-1: $\text{V}_2\text{O}_5:\text{CeO}_2$ =93:2:5	92	96	97	0.7

15 CLAIMS

1. A catalyst for the purification of waste gas by the removal of nitrogen oxides which comprises (A) from 80 to 95% by weight of an oxide obtained by thermal treatment of a binary hydrous oxide of titanium and silicon, a binary hydrous oxide of titanium and zirconium or a ternary hydrous oxide of titanium, zirconium and silicon in the presence of sulfuric acid or ammonium sulfate, (B) from 0 to 5% by weight of vanadium oxide, and (C) from 1 to 15% by weight of an oxide of tungsten, molybdenum, tin or cerium. 15
2. A catalyst according to claim 1, wherein the component (A) comprises (a) from 40 to 95 parts of titanium, (b) from 60 to 5 parts of silicon or zirconium, and (c) from 1.2 to 7 parts of sulfur, by atomic ratio. 20
3. A catalyst according to claim 1 or claim 2, which comprises from 85 to 95% by weight of (A), from 0 to 3% by weight of (B) and/or from 3 to 12% by weight of (C). 25
4. A catalyst according to any preceding claim, wherein the component (A) is obtained by thermal treatment of a binary hydrous oxide having a composition of $\text{Ti:Si} = 40$ to $95:60$ to $5:1.2$ to 7 by atomic ratio. 25
5. A catalyst according to any of claims 1 to 3, wherein the component (A) is obtained by thermal treatment of a ternary hydrous oxide compound having a composition of $\text{Ti:(Si+Zr):S} = 40$ to $95:60$ to $5:1.2$ to 7 by atomic ratio. 30
6. A catalyst according to any preceding claim, wherein the component (A) is composed of (a) from 50 to 90 parts of titanium, (b) from 50 to 10 parts of silicon and/or zirconium, and (c) from 1.5 to 5 parts of sulfur, by atomic ratio. 30
7. A catalyst according to any preceding claim, wherein the component (A) has a BET surface area of not less than $60 \text{ m}^2/\text{g}$. 35

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